学校编码：10384　　分类号_____密级 _____
学号：20720131150053　　UDC _____

厦门大学

硕 士 学 位 论 文

几种天然高分子电解质的粘度行为及其应用于复合材料的制备

Viscosity behaviors of Natural Polyelectrolytes and Preparation of Polymer Nanocomposites

廖芸英

指导教师姓名：　熊 晓 鹏　教 授
专 业 名 称：　高分子化学与物理
论文提交日期：　2016 年 5 月
论文答辩时间：　2016 年 5 月
学位授予时间：　2016 年　　月

答辩委员会主席：_____
评　　阅　　人：_____

2016 年 4 月

厦门大学学位论文原创性声明

本人呈交的学位论文是本人在导师指导下,独立完成的研究成果。本人在论文写作中参考其他个人或集体已经发表的研究成果，均在文中以适当方式明确标明，并符合法律规范和《厦门大学研究生学术活动规范（试行）》。

另外，该学位论文为（　　）课题（组）的研究成果，获得（　　）课题（组）经费或实验室的资助，在（　　）实验室完成。（请在以上括号内填写课题或课题组负责人或实验室名称，未有此项声明内容的，可以不作特别声明。）

声明人（签名）：

年　　月　　日

厦门大学学位论文著作权使用声明

本人同意厦门大学根据《中华人民共和国学位条例暂行实施办法》等规定保留和使用此学位论文，并向主管部门或其指定机构送交学位论文（包括纸质版和电子版），允许学位论文进入厦门大学图书馆及其数据库被查阅、借阅。本人同意厦门大学将学位论文加入全国博士、硕士学位论文共建单位数据库进行检索，将学位论文的标题和摘要汇编出版，采用影印、缩印或者其它方式合理复制学位论文。

本学位论文属于：

（　　）1.经厦门大学保密委员会审查核定的保密学位论文，于　　年　　月　　日解密，解密后适用上述授权。

（　　）2.不保密，适用上述授权。

（请在以上相应括号内打“√”或填上相应内容。保密学位论文应是已经厦门大学保密委员会审定过的学位论文，未经厦门大学保密委员会审定的学位论文均为公开学位论文。此声明栏不填写的，默认为公开学位论文，均适用上述授权。）

声明人（签名）：

年　月　日

摘 要

材料作为现代科学技术的三大支柱之一，承担着人类社会发展的学科使命。而天然高分子电解质，突破传统高分子的发展困境，结合天然资源、高分子和电解质三种优势，已经成为材料科学、生物、医学等诸多领域内的研究热点。然而，对高分子电解质尤其是天然高分子而言，虽已取得一定研究进展，但在一些基础领域仍亟待更深入的理解。比如，高分子电解质的构象如何随其浓度变化、外加盐如何改变溶液的热力学性质等。粘度法作为表征高分子最基本、最重要和便捷的方法之一，常用于研究高分子电解质的溶液行为，如测定其特性粘数。传统方法如 Huggins 方程、Fuoss-Straus 方程等通过外推至无限稀释获得截距而求得特性粘数，但 0/0 型外推过程将引入难以避免的极低浓度下实验过程中的不确定因素，而带来巨大误差。本论文主要采用一种普适性的特性粘数确定方法来描述海藻酸钠、羧甲基纤维素钠和牛血清蛋白这三种天然高分子电解质在不同外部条件下的粘度行为，以此探究其溶液特性和热力学性质。并在此基础上，以球形牛血清蛋白诱导制备多级结构 ZnO 微球。具体研究工作如下：

不同外加盐对海藻酸钠和羧甲基纤维素钠的粘度行为的影响

配制不足以使海藻酸钠(SA)和羧甲基纤维素钠(NaCMC)凝胶化的不同浓度的 NaCl 水溶液和 $CaCl_2$ 水溶液，分别以它们和去离子水为溶剂配制 SA 溶液(约 0.45 g/L)和 NaCMC 溶液(约 0.5 g/L)。用乌氏粘度计通过逐步稀释法测定其相对粘度，以 $\ln\eta$ 对浓度 c 作图，实验数据经 Wolf 方程拟合，得到 SA 和 NaCMC 的特性粘数$[\eta]$和各项参数，以此探究不同外加盐(Na^+或 Ca^{2+})对无限稀释状态的 SA 溶液和 NaCMC 溶液的粘度行为的影响。就体系浓度及盐度对 SA 溶液和 NaCMC 溶液粘度的影响及 SA 和 NaCMC 的$[\eta]$对比，揭示出由 Ca^{2+}引起的单个 SA 线团或 NaCMC 线团尺寸收缩的效果好于 Na^+，这可能是因为无限稀释时，Ca^{2+}优先与高分子阴离子相互作用而形成分子内交联。对 SA 溶液和 NaCMC 溶液的特定特性粘数$\{\eta\}$和线团重叠参数 Ω 进行分析，不难发现，比起去离子水体系，存在 Na^+的 SA 溶液或 NaCMC 溶液，其$\{\eta\}/[\eta]$的组成依赖关系下降趋势

更为缓慢；而当二价 Ca^{2+}存在时，SA 溶液和 NaCMC 溶液的$\{\eta\}/[\eta]$的组成依赖关系呈上升趋势，并达到一个最大值；并进行相应的探讨。

_pH_对牛血清蛋白的粘度行为的影响

分别以醋酸缓冲溶液(*pH*=3.8、4.6、6.0)、磷酸二氢钠缓冲溶液(*pH*=6.7、8.4)和碳酸氢钠缓冲溶液(*pH*=10.1、11.5)为溶剂，配制牛血清蛋白(BSA)溶液(约 4 g/L)。用乌氏粘度计通过逐步稀释法测定其相对粘度，实验数据经 Wolf 方程拟合，得到 BSA 的特性粘数$[\eta]$和各项参数，以此探究体系 *pH* 对无限稀释的 BSA 溶液的粘度行为的影响。就体系 *pH* 及浓度对 BSA 溶液粘度的影响及 BSA 特性粘数$[\eta]$的组成依赖关系，揭示出 BSA 线团在近 *pI* 溶剂中高度紧缩甚至缠结，在中性溶剂中呈舒展构象，在弱酸弱碱溶剂中呈部分膨胀构象，而在强碱溶剂中则尺寸收缩。这应该与 BSA 的溶液性质有关：即不同 *pH* 下，高分子阳/阴离子和两性高分子离子的比例、分子表面/内部电荷聚集状况和构象变化会引起 BSA 线团尺寸变化。对 BSA 溶液的特定特性粘数$\{\eta\}$和线团重叠参数 Ω 进行分析，发现比起中性溶剂，弱酸弱碱溶剂中的 BSA，其$\{\eta\}/[\eta]$的组成依赖关系下降更为缓慢；而近 *pI* 或强碱溶剂中，BSA 溶液$\{\eta\}/[\eta]$的组成依赖关系呈上升趋势；并作出了相应解释。

牛血清蛋白诱导制备多级结构氧化锌微球

将锌氨溶液、牛血清蛋白(BSA)溶液和无水乙醇根据一定比例混合，得到的原液通过水热反应，形成具有凸状结构的 ZnO 微球。经空气中 600 ℃ 热处理，成功制备由纳米 ZnO 颗粒组装形成的多级结构 ZnO 微球。SEM 和 TEM 结果显示，微球的宏观尺寸约为 150 nm-200 nm，它由尺寸约为 25 nm 的 ZnO 颗粒堆积组装形成。经 XRD 证实，本实验方法制得的 ZnO 晶体为典型的六角纤锌矿晶体结构。通过调节 BSA 浓度来优化 ZnO 微球的制备条件。结合配位化学，通过中性和碱性溶剂对照实验，探究氨水、BSA 对形成凸状结构 ZnO 微球的贡献；研究了 BSA 对凸状结构 ZnO 微球晶体生长的诱导机制，认为其是 ZnO 微晶与 BSA 之间选择性结合、相互作用的结果。改变热处理条件，依据 XRD、SEM、TEM 照片和 FTIR 谱图，探究多级结构 ZnO 微球的自组装机理，

认为其是不同大小的 ZnO 纳米颗粒聚集体经 BSA 粘结，并进一步在 600℃ 空气中生长形成的。最后，利用多级结构 ZnO 分别对亚甲基蓝和罗丹明 B 进行紫外光降解研究，发现其对罗丹明 B 有着比亚甲基蓝更好的光催化降解活性。

关键词：天然高分子电解质；海藻酸钠；羧甲基纤维素钠；牛血清蛋白；粘度行为

Abstract

As an important support of modern science and technology, materials are undertaking the mission promoting the development of human society. Among the materials, natural polyelectrolytes, combining the advantages of natural sources, polymers and electrolytes, have become one of the most interested topics in materials science, biology and medical science. For polyelectrolytes especially natural polyelectrolytes, although considerable progress has been reached, the understanding of their behaviors in some fundamental fields is still a challenge. For example, the effect of concentration increasing on the conformation of polyelectrolytes or that of extra salts in polyelectrolytes solution on the thermodynamic properties are still not clear. Viscometric method, as an important and convenient method for polymer characterization, is usually applied to study the solution behavior of polyelectrolytes such as the determination of intrinsic viscosity. Traditional methods such as Huggins equation and Fuoss-Strauss equation often require extrapolating viscosity vs. concentration to infinite dilution in order to obtain intrinsic viscosity. Those relations are in all cases zero-divided-by-zero regressions at infinite dilution, and would bring huge errors in the obtained intrinsic viscosity because of the inevitable uncertainties during experimental procedure. In this work, we employed a universal method for the determination of intrinsic viscosity with high precision. The new method can describe the viscosity behavior of sodium alginate, sodium carboxymethyl cellulose and bovine serum albumin under different external conditions. Based on those calculations, the specified thermodynamic properties of the polyelectrolytes were discussed. Moreover, a hierarchically structure ZnO microspheres were prepared under the induction of the bovine serum albumin. More details of the work are as follows:

Effects of extra salt type on viscosity behaviors of sodium alginate and carboxymethyl cellulose

The NaCl solutions and $CaCl_2$ solutions with different concentrations were prepared, in which the gelation of alginate (SA) and sodium carboxymethyl cellulose (NaCMC) were avoided. SA and NaCMC were dissolved in the above solution and deionized water, and their concentration are about 0.45 g/L and about 0.5 g/L,

respectively. The intrinsic viscosity [η] and parameters were obtained by the model of experimental data measured by Ubbelohde capillary viscometer according to Wolf equation, which is in order to explore the effects of extra salt (Na^+ or Ca^{2+}) on viscosity behaviors of dilute SA and NaCMC solution. The influences of concentration and salinity on the relative viscosity and the comparison in terms of salt molarities discloses that Na^+ shrinks the dimensions of individual polyelectrolyte coils - as measured by [η] - considerably less efficient than Ca^{2+}, probably due to the preferential interaction of Ca^{2+} with the charged macromolecules. In case of the specific intrinsic viscosity {η} and coil overlap parameter Ω, the composition dependences of {η}/[η] decreases slower in salinity solvents than in pure water, which is attributed to less pronounced shielding of extra salt than the self-shielding of the polyelectrolytes. However, the composition dependences of {η}/[η] in the presence of extra $CaCl_2$ increase and passes a maximum with polymer concentration rising, which is considered to be associated with the reestablishment of Ca^{2+} ions inside and outside of individual coils.

Effects of *pH* on viscosity behaviors of bovine serum albumin

The bovine serum albumin (BSA) were dissolved in the acetic acid buffer solution (*pH* = 3.8, 4.6, 6.0), sodium dihydrogen phosphate buffer solution (*pH* = 6.7, 8.4) and sodium bicarbonate buffer solution (*pH*=10.1, 11.5), respectively. The concentration of BSA solutions was about 4 g/L. The intrinsic viscosity [η] and parameters were obtained by the model of experimental data measured by Ubbelohde capillary viscometer according to Wolf equation, which is in order to explore the effects of *pH* on viscosity behaviors of dilute BSA solution. The influences of concentration and salinity on the relative viscosity and the comparison in terms of salt molarities illustrate that the BSA coil highly shrink, and even tangle in the solvent near *pI*, and the conformation of BSA stretches in neutral solvent, partially expand in weak acid or weak base solvents, shrink in alkali. The above phenomenon may be associated with the solution properties of BSA. Because of the proportion of polycations, polyanions and polyamphion, charge aggregated condition and the conformation change in the solutions with different *pH*, the coil size of BSA vary, resulting in the diverse viscosity behavior. In terms of the specific intrinsic viscosity {η} and coil overlap parameter Ω, the composition dependences of {η}/[η] decrease slower in weak acid or weak base solvents than in neutral solvent. However, the

composition dependences of $\{\eta\}/[\eta]$ in alkali increase with polymer concentration rising.

Preparation and characterization of hierarchical ZnO microspheres induced by BSA

The hierarchical ZnO microsphere assembled by ZnO nanoparticles were successfully prepared by hydrothermal method induced by BSA. The range of microspheres size is 150 nm-200 nm, and the size of ZnO nanoparticles is about 25 nm. The crystalline structures of hierarchical ZnO microspheres are in wurtzite phase, which were characterized by XRD. The preparation conditions of ZnO microsphere were optimized through tuning the contents of BSA. Combined with coordination chemistry theory and the control experiment in neutral or alkali solvents, the contribution of ammonia water and BSA to the formation of ZnO with bulges and the growth mechanism of ZnO crystals were investigated. The results indicated that the different ZnO crystals were formed due to the selective conjunction between BSA micelles and ZnO microlites. Furthermore, according to the results of XRD, SEM, TEM and FTIR, and by changing the calcining condition, we propose the self-assembly mechanism of hierarchical ZnO microspheres. By continually bonding between BSA micelles and ZnO nanoparticles aggregates to assemble ZnO microspheres, and further growing in the air in 600 ℃, we can obtain the hierarchical ZnO microspheres. Therefore, here, a facile method of preparing hierarchical metallic oxide materials is provided. Finally, the photocatalytic activity of the hierarchical ZnO microsphere was studied by measuring the photo-degradation of methylene blue and rhodamine B.

Keywords: Natural Polymer Polyelectrolytes; Sodium Alginate; Sodium Carboxymethyl Cellulose; Bovine Serum Albumin; Viscosity Behavior

目 录

Table of Contents